ANOMALOUS DISPERSION OF X-RAYS IN CALCITE

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Anomalous Dispersion of X-Rays in Calcite

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The index of refraction of calcite ($CaCO_3$) for x-rays has been investigated in the wave-length range from 2880 to 3550 x.u., which includes the K absorption edge of calcium. The method is such that all of the incident beam enters the crystal through an artificial face, ground so that after reflection from the (100) planes a part of the beam emerges through this face at a sufficiently small angle to be refracted appreciably. At the same time another part of the beam emerges from a cleavage face at a large angle and is refracted only a little. The separation between the two is a measure of the index. The continuous spectrum is used rather than emission lines, thus enabling measurements to be made as closely spaced in wave-length and as near the absorption edge as is desired. The absolute accuracy of the method in its present form is probably not great, but the relative accuracy is sufficient to show a distinct dip in δ/λ^2 in the vicinity of the absorption edge. A comparison is made with Hönl's theoretical curve.

INTRODUCTION

BECAUSE the index of refraction of all substances for x-rays is very nearly unity, the refractive bending of an x-ray beam has a measurable magnitude only when the angle between the beam and the interface is very small. Bergen Davis first suggested grinding an artificial face on a crystal in order that an x-ray undergoing Bragg reflection might make a small angle with the surface. The experiments of Davis and Hatley[1, 2] gave the first quantitative determinations of the index of refraction. Variations of this method have been used by Lindsay and his collaborators[3, 4] to measure the index of cerussite ($PbCO_3$). Retaining the idea of a small angle at the interface, but not using Bragg

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[1] C. C. Hatley and Bergen Davis, Phys. Rev. **23**, 290 (1924).
[2] C. C. Hatley, Phys. Rev. **24**, 486 (1924).
[3] H. C. Hoyt and G. A. Lindsay, Phys. Rev. **49**, 498 (1936).
[4] J. E. Field and G. A. Lindsay, Phys. Rev. **51**, 165 (1937).

reflection, Lärsson[5] and Bearden and Shaw[6] have obtained accurate results with right-angled prisms of various substances.

Outline of the Present Method

In this investigation the index of refraction of calcite ($CaCO_3$) was studied in the region of the K absorption edge of calcium. A new adaptation of Davis' method was employed. A crystal with an artificial or bevelled face was used, the entire x-ray beam entering the crystal through this face. Upon emerging, one component came through the bevelled face at a sufficiently small angle to be refracted appreciably, while the other came out through a cleavage face at a large angle and was bent only a little. The second component furnished a reference from which the bending of the first could be measured. This is illustrated in Fig. 1.

The crystals were prepared by grinding off a corner and optically polishing the resulting face AB (Fig. 2).[7] This makes an angle φ with the (100) planes, as shown in Fig. 1. After the bevelled face had been polished the crystal was cleaved along CD. It was necessary that the edge at D between the cleavage and bevelled faces be sharp and distinct for a distance of at least a few millimeters. The crystals were prepared

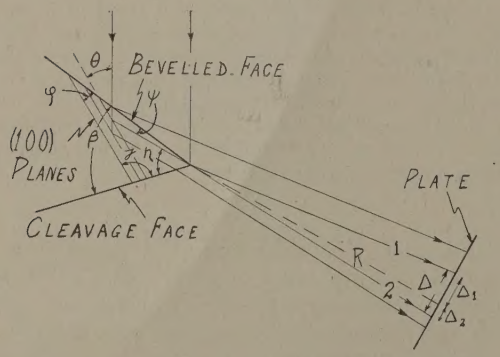

Fig. 1. Geometry of the x-rays in the crystal. This shows the quantities used in the derivation of the expression for $\delta = 1 - n$.

[5] Axel Lärsson, *Dissertation*, Uppsala (1929).
[6] J. A. Bearden and C. H. Shaw, Phys. Rev. **46**, 759 (1934).
[7] Emission lines reflected from the bevelled face were as sharp as those from the cleavage face, which shows that the polish was satisfactory and that there was very little powder or mosaic structure on the surface.

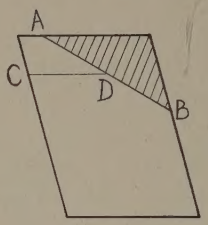

Fig. 2. In preparing the calcite crystals, the shaded part was ground off and the face AB polished. Then the crystal was cleaved along CD.

by the Bryden Company of Waltham, Massachusetts.

The investigation was carried out with a Siegbahn vacuum spectrometer having a radius of 181.6 mm and a slit width of 0.10 mm. Before being mounted in the instrument each crystal was examined microscopically in order to be certain that the edge was sufficiently sharp for use. It was then set up with the sharp part of the edge accurately in the axis of the spectrometer. Thus the distance from the edge of the crystal to the photographic plate remained constant as the crystal was rotated about the axis of the instrument. Only radiation reflected from the best parts of the edge was considered.

All measurements were made with the continuous x-ray spectrum, with known emission lines for reference to determine the wave-length being refracted. This permits one to take many points at very small wave-length intervals, and in particular it allows an indefinitely close approach to the wave-length of the absorption edge, where the unit decrement falls off sharply.

Optics and Geometry of the Problem

The emerging ray *1* makes a small angle $\psi = \theta - \varphi$ with the bevelled face (Fig. 1). Throughout the work this angle ranged from about 1° to 5°, and in the following development we may with sufficient accuracy take its cosine to be unity and its sine and tangent equal to the angle. Ray *2* emerges from the cleavage face at a much larger angle η. If there were no refraction both rays would follow the direction of the broken line from the edge of the crystal to the plate. We see that the angular deviation of ray *1* is Δ_1/R, where R is the radius of the spectrometer, and the deviation of ray *2* is Δ_2/R. If now $\delta = 1 - n \ll 1$,

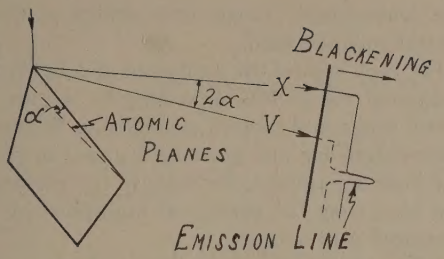

FIG. 3. Ray diagram illustrating the measurement of the deviation angle α by means of x-radiation and visible light.

where n is the index of refraction, it may easily be shown that $\Delta_1=\delta R/\psi$, and $\Delta_2=\delta R/\tan\eta$. The separation actually measured on the photographic plate is

$$\Delta_1+\Delta_2=\delta R(1/\psi+1/\tan\eta).$$

Solving this equation for δ and dividing by λ^2 we see that

$$\delta/\lambda^2=(\Delta/R\lambda^2)(\psi\tan\eta/(\psi+\tan\eta)). \qquad (1)$$

The Bragg equation, $\lambda=2d\sin\theta$, will furnish the value of θ when the wave-length is known.[8] The measurement of φ will be described below. The angle made with the cleavage face is given by $\eta=180°-\theta-\gamma$. The value of γ obtained by Beets[9] was used.

Because ψ is very small, it is necessary to know both θ and φ with great accuracy. Bearden and Roseberry[10] have reported deviations of the cleavage faces of calcite from the atomic planes supposedly parallel to them. If such a deviation existed here the simple relation $\varphi=180°-\beta-\gamma$ would not be accurate. In order to measure this deviation angle for crystal D the crystal was turned for reflection from the cleavage face. An x-ray exposure was made, the crystal being in such a position that an emission line appeared on the plate. The plate was also blackened by the continuous spectrum, the intensity of which fell off sharply at ray X (Fig. 3), the ray reflected just at the edge of the crystal. Next, a second plate was exposed to x-rays, but for a shorter time—sufficient to show the line but not the continuous background. While this second plate was still in position, the anode was removed and visible light allowed to fall on the crystal through the slit. As with the x-radiation, the blackening decreased rapidly beyond the ray V coming from the edge. Since the x-rays were reflected by the atomic planes and the visible light by the actual surface of the crystal, the angular separation between the two extreme rays (as measured on the plates, with the emission line as reference) is just twice the deviation angle α between the planes and surface. α was found to be 43″. β was measured with a goniometer. We may now calculate $\varphi=180°-(\alpha+\beta+\gamma)$. The angle η is of the order of magnitude of 45°, so there was no need to correct it for the deviation angle.

For crystals E and F, φ was obtained directly in a manner very similar to that described above. Here it was necessary to turn the plate through a large angle approximately equal to 2φ between the x-ray and visible light exposures. By a proper choice of this angle the two blackened regions could be made to occur several millimeters apart, so that one plate was sufficient and no reference emission line was necessary. The plate circle of the spectrometer was observed through two microscopes about 180° apart, and the average of the differences between the initial and final readings taken as the angle through which the plate was turned. If we call this angle A, and the separation between the blackened regions D, then $\varphi=\frac{1}{2}(A\pm D/R)$; the sign is determined by the relative placing of the two regions.

Determination of the Refracted Wave-Length

The wave-length of the ray refracted at the edge of the crystal was determined from that of a known emission line. This line was reflected according to the Bragg Law, but emerged through the bevelled face at some distance from the edge. The difference in wave-length $d\lambda$

[8] With the continuous spectrum, it is possible to measure refraction only for first-order reflection. If radiation which would be reflected in second order were present, it would emerge at the same angle, but δ would be only one-fourth as great, so that at the plate the ray would fall between the refracted and reference components of the first-order radiation. The result would be merely to blur the position of ray I. To prevent this the tube voltage was always kept so low as barely to excite radiation of this wave-length.

[9] H. N. Beets, Phys. Rev. 25, 624 (1925).

[10] J. A. Bearden and H. H. Roseberry, Phys. Rev. 48, 110 (1935).

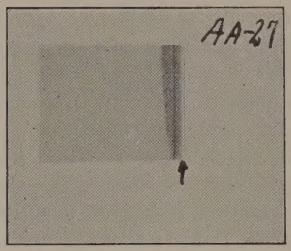

FIG. 4. Plate taken with Crystal *F* at 2813 x.u. The sharp line at the extreme right is caused by the radiation emerging from the cleavage face (ray *2* of Fig. 1). The arrow points to the separation Δ between the reference and refracted components. The line in the center is Sb $L\gamma_1$, λ2845 x.u., reflected from the bevelled face. Wave-length increases from right to left.

between this line and the ray emerging from the bevelled face just at the edge is given by

$$d\lambda=(d\cos\theta/R)(1+\tan\varphi/\tan\theta)ds, \qquad (2)$$

where ds is the separation on the plate. The wave-length of the ray at the edge is obtained by subtracting $d\lambda$ from the wave-length of the line. It was found that sufficient accuracy was obtained if the value of θ for the line were used in the expression (2), and the $d\theta$ corresponding to $d\lambda$ was neglected. Corrections for refraction were negligible even when the line was observed in the second order. The wave-lengths of the lines and the value of the grating constant $d(=d_{(100)})$ were taken from Siegbahn.[11]

METHODS OF ASSEMBLING DATA

Figure 4 is a photograph of one of the plates. The dark background is the blackening due to the continuous spectrum emerging from the bevelled face. Near the right-hand edge is seen a white line; this is the region between the rays *1* and *2* of Fig. 1. Beyond is a distinct dark line, caused by the radiation which passed through the crystal and out through the cleavage face. The width of the white line is the quantity Δ in the development above. It was measured on a comparator. For ψ less than about 1° the left side of the white line was too indistinct for measurement, and for ψ greater than about 5° the width was too small. These limits determined the wave-length range over which any one crystal could be used.

For each crystal the coefficient of Δ in (1) was computed for a few wave-lengths within the useful range and plotted graphically. When the wave-length for one plate or a group of plates had been determined, the value of this coefficient was read from the curve and multiplied by the measured Δ to find δ/λ^2.

With crystal *D*, points were taken at very small wave-length intervals from 2986 x.u. to 3267 x.u. The value of δ/λ^2 was found for each plate, then they were grouped and averaged. The wave-length range included in a group was 5 x.u. near the absorption edge, increasing to more than 40 x.u. at some distance away. For the work with crystals *E* and *F*, whose useful wave-length ranges were higher and lower, respectively, than that of crystal *D*, plates were taken in groups. Each group covered a wave-length range of some ten or twenty x.u., but was separated from its neighboring groups by considerably more. Within each group, the wave-lengths and Δ's were averaged, and a single value of δ/λ^2 was obtained. The averaged values appear in Table I, and they are plotted in Fig. 5.

The solid curve of Fig. 5 represents Hönl's theoretical expression[12] for δ/λ^2. This was obtained from the classical value by multiplying the term which represents the dispersion due to the *K* electrons by the hydrogenic oscillator strength as developed by Sugiura.[13] This is then integrated over the continuous spectrum from the frequency of the absorption edge to infinity. Analytically the result is given by

$$\delta/\lambda^2=\frac{Ne^2}{2\pi mc^2}\left\{1+\frac{N_{Ca}}{N}\frac{2^7\exp(-4)}{9}\lambda^2\times\left[\frac{4}{(1-\Delta_k)^2}\left(1+x^2\log\left|1-\frac{1}{x^2}\right|\right)-\frac{1}{(1-\Delta_k)^3}\left(\frac{2}{3}+2x^2+x^3\log\left|\frac{x-1}{x+1}\right|\right)\right]\right\}. \qquad (3)$$

Here e and m are the charge and mass of the electron, c the velocity of light, and $x=\lambda/\lambda_k$, where λ_k is the wave-length of the absorption

[11] M. Siegbahn, *Spektroskopie der Röntgenstrahlen*, Berlin (1931).

[12] H. Hönl, Zeits. f. Physik **84**, 1 (1933).

[13] Y. Sugiura, J. de phys. et le rad. **8**, 113 (1927).

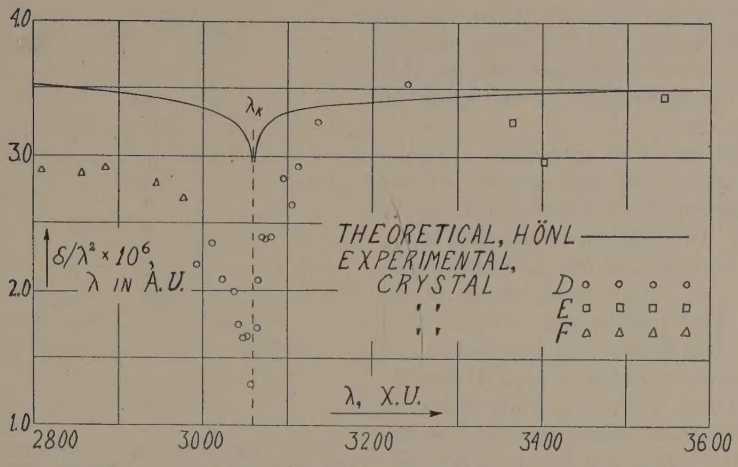

FIG. 5. The averaged experimental points, together with Hönl's theoretical curve, Eq. (3).

edge. N_{Ca} is the number of calcium atoms per cm^3 and $N = \Sigma N_i Z_i$. Here N_i is the number per cm^3 of atoms having the effective atomic number Z_i. By effective atomic number is meant the number of electrons which do not contribute to the K dispersion. This term thus includes all the electrons of carbon and oxygen, the L, M, etc. electrons of calcium, plus 0.59 K electrons per calcium atom which, from the value of the integrated oscillator strength, do not take part in K dispersion. Δ_k is a term containing screening and relativity corrections.

RESULTS AND DISCUSSION OF ERRORS

The values of δ/λ^2 obtained experimentally fall below Hönl's curve, especially on the short wave side of the absorption edge. Also the dip in the region of the edge is wider and deeper. Lärsson's[5] experimental results are the only ones which have been published with which a comparison may be made. His values agree very well with Hönl's on the short wave side, but fall a little low for longer wave-lengths. Because of uncertainties in the measurement of the separation between the refracted and reference components, it may well be that the present method does not give the absolute magnitude of the refraction. However, in regions in which data were obtained with two different crystals the separation and distinctness of the two components differed considerably on the plates taken with one crystal from those with the other.

TABLE I. *Average values of δ/λ^2. To show the spread of values for the individual plates there are given in the right-hand section of the table the individual values of δ/λ^2 for the group at 3094 x.u.*

NUMBER OF PLATES AVERAGED	WAVE-LENGTH (X.U.)	$\delta/\lambda^2 \times 10^6$
Crystal F, $\varphi = 26° 29.3'$		
4	2811	2.89
4	2858	2.87
1	2886	2.91
5	2947	2.80
1	2978	2.69
Crystal D, $\varphi = 28° 28.3'$		
2	2993	2.20
3	3011	2.35
3	3024	2.09
4	3037	1.99
4	3042	1.75
3	3048	1.65
3	3052	1.66
4	3056	1.30
4	3064	1.72
4	3066	2.08
2	3071	2.40
2	3076	2.39
2	3081	2.40
6	3094	2.84
5	3107	2.63
2	3113	2.93
3	3139	3.26
4	3241	3.54
Crystal E, $\varphi = 32° 4.5'$		
6	3365	3.25
8	3404	2.96
7	3546	3.43

PLATE	WAVE-LENGTH (X.U.)	$\delta/\lambda^2 \times 10^6$
Y-19	3093	2.70
20	3093	2.90
X-72	3094	2.57
71	3095	2.84
73	3095	2.93
Y-18	3096	3.07

Yet the values of δ/λ^2 obtained from the two agree well. This shows that the plates were all measured in the same manner, and indicates that the form of the dependence of refraction on wave-length is correct.

The principal source of error is in the comparator measurement of the position of the refracted component of the beam, which always appeared fuzzy. This position corresponds to ray *1* in Fig. 1. The causes of this fuzziness are as follows: In Fig. 6, S represents the slit of the spectrometer. Two parallel rays A and B of the same wave-length strike the bevelled face of the crystal and are reflected as rays A' and B'. Actually, of course, there is a finite beam incident upon the crystal; these rays merely define its limits. All the rays in this beam are reflected from the crystal. At the same time a ray C of slightly shorter wave-length may be incident upon the crystal at a smaller angle and be reflected as ray C', which falls outside the beam defined by A' and B'. The blackening at C' will be less than that at A' because it is caused by radiation coming from only a part of the slit. Thus as we go from A' toward shorter wave-lengths, the blackening diminishes not sharply, but gradually, as less and less of the slit contributes to it.

Also, since beams of longer wave-lengths reflected from the bevelled face do not emerge at the edge, the extent of the crystal contributing to their intensities is determined by absorption rather than by a limiting ray passing through the edge. These beams are therefore stronger than $A'B'$, and we have a second effect producing a gradual diminution of the blackening. Moreover, the area *abc* contributing to the beam $A'B'$ diminishes rapidly as the crystal is turned to refract shorter wave-lengths, while the absorption-limited regions contributing to the longer wave-lengths do not. Thus the indistinctness of the position of ray A' (the same as ray *1* of Fig. 1) increases as the refracted wave-length is decreased. At the same time the separation from the unrefracted component increases, so that the relative accuracy of measuring Δ does not change rapidly, but eventually, as was mentioned above, a lower limit of ψ is reached beyond which measurements cannot be made.

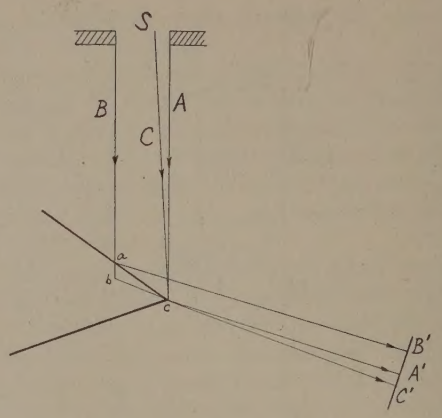

FIG. 6. A ray C having a wave-length slightly less than that of A and B causes a gradual decrease in blackening at A'.

Microphotometer curves were taken for a few plates, but measurements of Δ obtained from them were no more consistent than those from the comparator. Positions on the plate would probably have been more distinct if a narrower slit had been used, but that would have increased the required exposure times unreasonably. As it was, most of the plates were exposed for about twenty hours, and few for as long as forty hours.

From the method described in this paper, refraction may be measured at any wave-length desired, in substances which form good single crystals having linear dimensions of at least a few millimeters. The faces used may be natural or artificial, provided only that it is possible to obtain a sharp edge between them parallel to some set of atomic planes.

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